THERMAL EFFECTS ON THE RAPID DEVOLITIZATION OF COAL

O. Morel and F. J. Vastola

Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

INTRODUCTION

One of the major difficulties in the calculation of the kinetics of coal pyrolysis under conditions of rapid heating is the determination of the temperature history of the coal during the pyrolysis event. The temperature at which the pyrolysis occurs when a particle of coal is injected into a hot environment is dependent on the rate of heat transfer to the particle surface and the rate at which heat is transported through the particle. This latter transfer is further complicated by the heat adsorbed or released by the pyrolysis reaction as well as phase changes that can occur within the particle. One method of obtaining data on the thermal response of coal under rapid heating conditions is to measure the variation in gas temperature when particles are injected into a hot gas environment where gas convection will play a significant role in the heat transfer process. By measuring local gas temperature in the vicinity of a particle injected into a hot environment the time of the heating-pyrolysis period can be measured and an estimate can be made of the relative contributions of gas convection and radiation to the process.

EXPERIMENTAL

Figure 1 illustrates the design of the captive particle isothermal flow reactor used in this investigation. Single or multiple particles of coal or char are placed on a solenoid controlled platform. A rapid withdrawal of the platform allows the particle(s) to fall into a preheated reaction environment. The time of entry into the reaction zone is detected by the perturbation of a light beam located at the entrance of the reaction zone. Preheated He was used as the gaseous pyrolysis environment. To detect temperature transients induced by sample injection a 0.13 mm cross section chromel-alumel thermocouple was placed in the reactor in such a manner that the samples after injection would be extremely close to the thermocouple tip. The thermocouple output was amplified and the resulting signal was digitized with a computer controlled 12-bit analog to digital converter. The converter had an acquisition time of 20 μs the sampling period used in this study was 1 ms. The coal used was PSOC-640 a HVA bituminous coal, its analysis is given in Table 1. Multiple coal particles in sized ranges of 80-220 μm in diameter and single particles of approximately 2 mm in diameter were used.

RESULTS AND DISCUSSION

Figure 2 shows the gas temperature in the vicinity of an injected 4.8 mg, 2 mm coal particle vs time. The reactor temperature was 1072 K and the gas environment was quiescent He. The second plot was obtained by reinjecting the 2.5 mg char particle resulting from the pyrolysis of the coal particle. The thermocouple is rapidly cooled on particle injection then is slowly reheated as the sample and the gas surrounding the sample approach the reactor temperature. The differences in the extent of the temperature perturbation between the coal and char are due to the change in mass resulting from the loss of VM from the coal and the endothermicity of the pyrolysis process. By slightly changing the position of the thermocouple for different runs, it was observed that the cooling effect was a localized phenomenon, taking place only in the very close neighborhood of the sample. This indicated that the bulk temperature of the gas remained constant during the pyrolysis-heating period.

TABLE 1

CHEMICAL DATA FOR HIGH VOLATILE A BITUMINOUS PSOC 640

PROXIMATE ANALYSIS

Analyses, Weight %	Dry	DMMF (Parr)
Ash	8.1	
Volatile Matter	37.3	39.6
Fixed Carbon	54.6	60.4
ULTIMATE ANALYSIS		
Ash	8.1	
Carbon	74.7	83.3
Hydrogen	5.2	5.8
Nitrogen	1.3	1.4
Sulphur	2.8	-
Oxygen (diff)	7.9	9.5

Energy transfer from a hot environment to a particle is by both gaseous convection and thermal radiation. The magnitude of the radiative transfer can be readily estimated. The maximum rate of radiant energy delivered to the particle by its surroundings is equivalent to the energy radiated by the particle at the temperature of its surroundings.

$$P = \sigma \varepsilon A T^4 \tag{1}$$

P = maximum radiative power, W
σ = Stephan-Boltzman constant, 5.67×10^{-8} W/m^2-K
ε = emissivity of particle, 0.7
A = area of particle, 1.36×10^{-5} m^2
T = reactor temperature, 1072 K

In this case $P = 0.71$ watts.

The amount of energy required to heat a particle of coal to the temperature of its environment when that temperature is sufficiently high to allow the pyrolysis to go to completion in a measurable time would be:

$$q = M_p C_p \Delta T + M_p \Delta H \tag{2}$$

where M_p is the mass of the particle, C_p is its heat capacity, ΔT the initial particle-environment temperature difference and ΔH is the heat of pyrolysis. If, for example, the 2 mm particle of the previous calculation was taken and the following characteristics assumed,

M_p = .0048 g
C_p = 1.6 J/g-K
ΔH = 700 J/g

the energy required to heat the particle from 300 K to 1072 K would be 9.29 J. If this particle was to be heated by radiation alone the heating time would be greatly in excess of that measured experimentally. For the single particle experiments the small contact area of a spherical particle contacting the silica surface of the reactor would tend to minimize the contribution of solid-solid heat conduction. Consequently the major reason for the shortening of the pyrolysis period from that calculated by radiative transfer alone is heat transfer via gas conduction.

A more exacting calculation can be made by making an energy balance for the particle taking into account convection, radiation, heat capacity and the heat of pyrolysis.

$$hA_p(T_g-T_p) + \sigma A_p \epsilon_p (T_w^4-T_p^4) + RH_p = M_p C_p dT_p/dt \tag{3}$$

The values used to model the 2 mm coal and char particles in Figure 2 are:

h = heat transfer coefficient, W/m^2-K
A_p = area of particle, 1.36×10^{-5} m^2
T_g = gas temperature, 1072 K
T_p = particle temperature, K
ϵ_p = particle emissivity, .7
T_w = wall temperature, 1072 K
R = pyrolysis rate, g/s
H_p = heat of pyrolysis of coal, 700 J/g
M_p = mass of particle, coal .0048 g, char .0025 g
C_p = particle heat capacity, J/g-K.

The heat capacities of coal and char as a function of temperature were obtained using the following equation:

$$C_p(T) = a + bT + cT^2 + dT^3 + eT^4 \tag{4}$$

Coal		Char	
a	- 0.685	a	2.673
b	9.235×10^{-3}	b	2.617×10^{-3}
c	-1.262×10^{-2}	c	1.169×10^{-5}
d	7.865×10^{-3}		
e	-1.85×10^{-12}		

The data used for fitting the equation for coal was extrapolated from that given by Merrick (1). The heat capacity of graphite (2) was used to approximate that of char. The rate of pyrolysis was assumed to be a first order reaction with a pre-exponential of 10^{-5}/s and an activation energy of 83.6 kJ/gmole.

This model was able to fit the temperature profile of a single coal particle and when setting the reaction term to zero the profile of the reinjected char particle. Figure 3 shows the experimental thermocouple response for the injection of a 2 mm diameter char particle, curve a, along with the calculated particle surface temperature profile, curve c. During the temperature perturbation experiments, the thermocouple was not measuring the temperature of the particle surface but rather a temperature intermediate between that and the temperature of the bulk gas,

$$T_{AV} = \frac{mT_g - nT_p}{m + n} \tag{5}$$

where n and m > 1. This equation represents a weighted average between the bulk gas and the particle surface temperature. These values were adjusted to fit the experimentally measured temperature, curve b. This correction does not change the calculated particle temperature history but only adjusts the calculation to give the gas temperature at a given distance from the particle surface. A similar calculation was used to model the data obtained from the injection of a 2 mm particle of coal, in this case the term accounting for the heat of pyrolysis is included in the model. Figure 4 shows the experimental data along with the adjusted model data. Other than the front edge of the experimental temperature curves good agreement is found between the model and the experimental data for both coal and char. The difference on the front edge is a consequence of the thermocouple being at reactor temperature prior to particle injection. In Figure 4 an inflection point can be n seen at the onset of rapid pyrolysis for both the experimental and calculated data.

The heat transfer coefficient, h which was used as the main adjustable parameter in the model, gave the best fit value, 123 W/m^2-s. Using this value the maximum convective heat flux would be,

$$q = hA\Delta T = 1.28 \text{ W} \tag{6}$$

this value is greater than the maximum radiative heat flux calculated in equation (1), 0.71 W. Under these circumstances convective heat transport is playing a dominant role.

Although many assumptions on values have to be made in the model, the values used in the calculation and the values obtained from the model do not appear unrealistic. However, the experimental measurement of significant temperature depressions in the vicinity of the injected particle is strongly indicative of the major role played by gas thermal transport.

When groups of small sized particles (80-500 μm) were introduced into the reactor, it was found that the heating times as measured by the thermocouple perturbation were only slightly shorter than that of a single particle of equivalent mass. If resistance to heat transfer occurs in the gas phase surrounding the particle, a temperature gradient would be expected to be found extending some finite distance from the particle surface to the bulk gas phase. If the particle density is such that the distance between particles would be less than the thickness of this boundary layer their inter particle interaction will result in longer heating times.

The modeling of the pyrolysis of coal under conditions of rapid heating relies on the knowledge of the temperature history of the coal during the pyrolysis process. From the results of this investigation it can be seen that a significant portion of the pyrolysis of a particle will occur at a temperature considerably lower than the reactor temperature. The assignment of the pyrolysis temperature is further complicated by intra particle temperature gradients. With the data currently available on heat capacity, thermal conductivity and heat of pyrolysis of coal, the temperature history of a rapidly heated coal particle cannot be reliably calculated a priori. It is essential that more accurate data on these properties be obtained.

ACKNOWLEDGEMENTS

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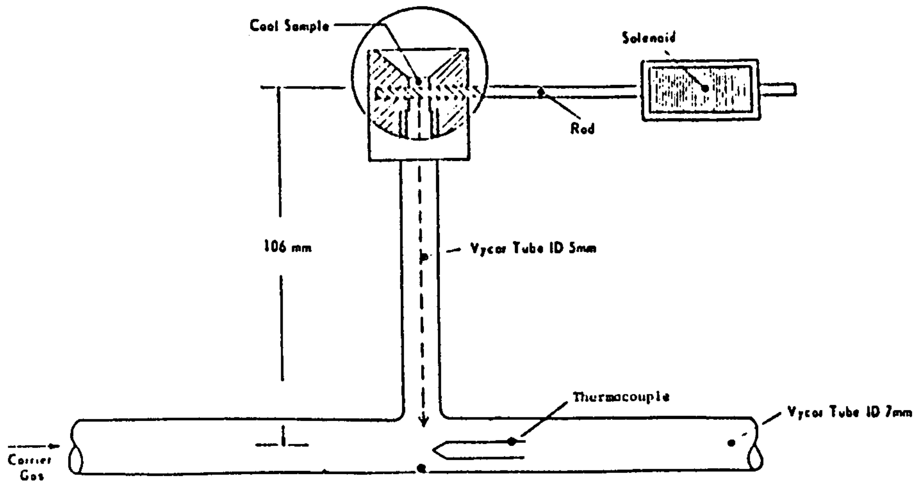

Figure 1. COAL INJECTION SYSTEM

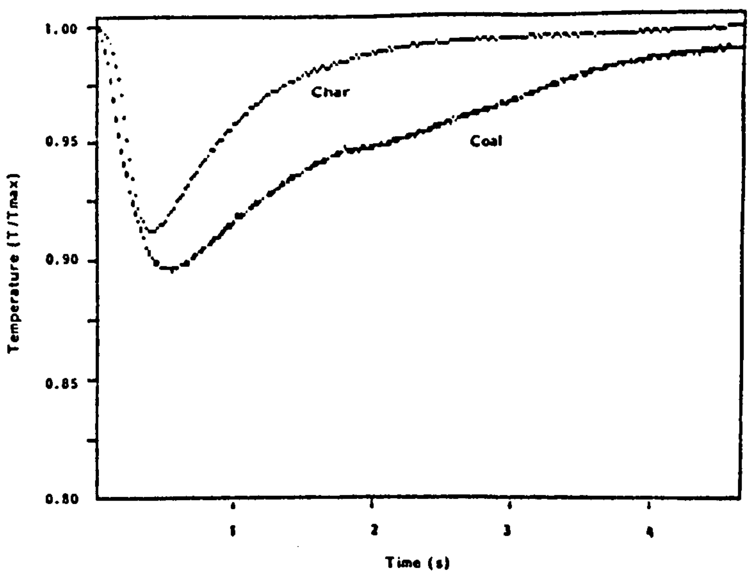

FIGURE 2. Temperature perturbation for single char and coal particles.

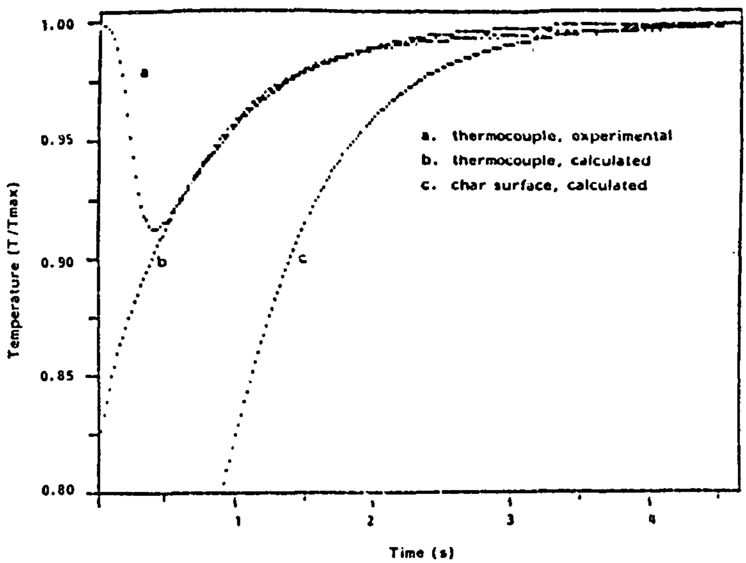

FIGURE 3. Temperature perturbation for a single char particle.

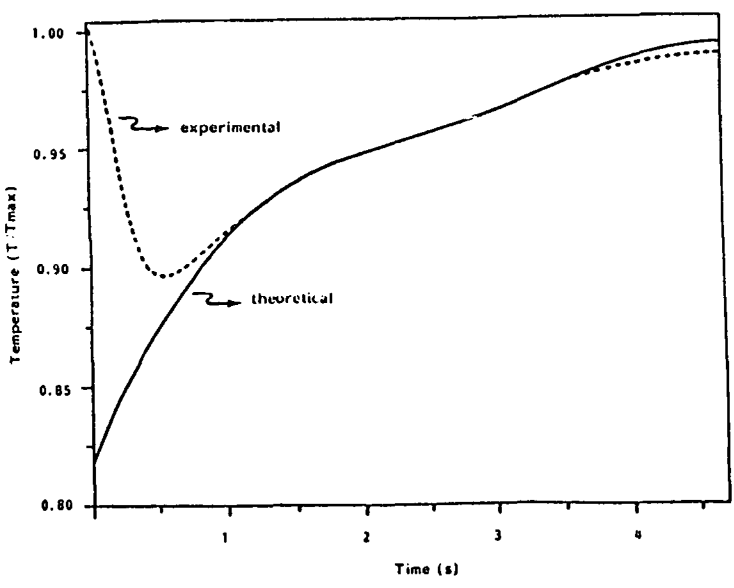

FIGURE 4. Temperature perturbation for a single coal particle.